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Oxidation of Butenes to Maleic Anhydride on $MnMoO_4$ Based Catalyst*

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The oxidation of *n*-butene-1 was carried out in a stirred tank reactor and in a pulse reactor using $MnMoO_4$ as a catalyst. This catalyst exhibits a fairly good selectivity to maleic anhydride. $MnMoO_4$ shows a polyfunctional nature; it is possible to distinguish the properties of isomerization, dehydrogenation, oxidation with oxygen insertion, and complete oxidation by varying parameters such as temperature, oxygen concentration and contact time.

The compositions of the products in the oxidation of *n*-butene-1 carried out in a pulse reactor are completely different in the presence and in the absence of oxygen, respectively. In the absence of oxygen, $MnMoO_4$ is a very selective catalyst in the dehydrogenation of *n*-butene-1 to butadiene. In the presence of oxygen, CO and CO_2 are the main products together with small amounts of maleic anhydride.

The selectivity of $MnMoO_4$ to butadiene formation has been attributed to the presence of Mo=O bonds which are responsible for dehydrogenation reactions.

A monocenter oxidation mechanism, accounting for the formation of CO, CO_2, and maleic anhydride, has been proposed in which the gaseous oxygen is considered to be adsorbed on the same center of the hydrocarbon.

INTRODUCTION

Maleic anhydride has lately been produced by new industrial processes from C_4 hydrocarbons; formerly it had been produced by more conventional processes from benzene (*1–5*). In general, the catalysts used consist of V and/or Mo oxides, mostly in the presence of other oxides, such as P_2O_5, WO_3, or CrO_3: they may be either supported or unsupported.

In our study on the oxidation of butenes to maleic anhydride carried out in a gradientless flow reactor, we have investigated the behavior of a $MnMoO_4$ catalyst which, as already known, is quite selective in the oxidation of methanol to formaldehyde (*6, 7*), and not selective in the oxidation and ammoxidation of propylene (*8*). The catalyst prepared by us gave yields in maleic anhydride and butadiene from *n*-butene-1 that are satisfactory although lower than those obtained in the presence of other known catalysts.

Oxidation runs of *n*-butene-1 in a pulse reactor both in the presence and in the absence of oxygen were also carried out in order to distinguish the role of lattice and adsorbed oxygen.

EXPERIMENTAL

1. *Apparatus*

The experimental apparatus is schematically shown in Fig. 1. Quarter inch or eighth inch standard stainless steel tubing was used; all fittings were made of Swagelok standard stainless steel and the valves were either needle or bellow type.

The reaction gases were obtained from

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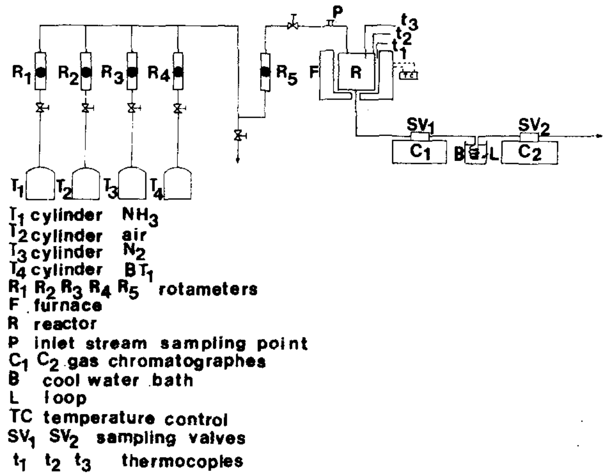

FIG. 1. Experimental apparatus.

high-pressure cylinders and passed through a series of pressure-regulating devices, metered over Brook glass rotameters, and mixed before entering the reactor. The mixed stream was split into two, one measured by a Gilmond rotameter and sent to the reactor; the other, after passing through a valve, was vented. The valve was used to control the first flow rate without changing the flow rate of each reactant. The reactor (a stirred-tank flow reactor) was constructed from a 316 stainless steel tube with an inside diameter of 55 mm and a height of 55 mm. It was put into a furnace where a stirrer maintained a satisfactory uniform temperature. Three thermocouples measured the temperature of the furnace, of the reactor walls, and of the gases inside, respectively.

Two twin-blade propellers mixed the gases and forced them through the catalyst basket (see Fig. 2). The basket, rotating simultaneously with the propellers, was a cylinder 25 mm in diameter and 25 mm in height. The top of the basket was conical in order to allow the gases to flow into it more easily. A water-cooled teflon packing was used to prevent leakage at the point where the shaft entered the reactor.

A reactor of this type was chosen because it guarantees the absence of heat and mass gradients due to transfer phenomena *(9–10)*, which necessarily occur in quite exothermic reactions as that studied by us.

A pulse microreactor has also been used. It consisted of ¼ inch stainless steel tube with a thermocouple inside to measure the catalyst temperature. The reactor was put inside a furnace and connected with the "outside column" device of a Fractovap C Carlo Erba gas chromatograph, as described later.

2. Analysis

Reactants and products were analysed by gas-chromatography using: (a) a Hewlett-Packard model 5750 chromatograph with a flame detector and a column

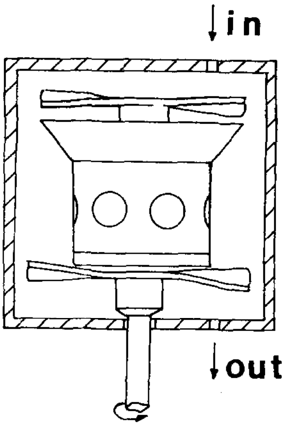

FIG. 2. Gradientless reactor.

of dinonylphthalate on celite (2 m long) kept at 140°C, for the analysis of oxidation products. (b) A Carlo Erba Fractovap C thermocouple detector gas chromatograph with a dimethylsulpholane 6.50 m long column for analysis of CO_2, butenes and butadiene at room temperature and with a molecular sieve 5 × 120 cm at room temperature for analysis of CO, N_2 and O_2. We had an "outside column" device on this model; when open, gases flowed into both the molecular sieve column and the dimethylsulpholane column for analysis; when closed, gases merely flowed through the dimethylsulpholane column. The outlet gases were passed through a tube heated to 150°C to prevent condensation of maleic anhydride and to a sampling valve heated, to 150°C to prevent condensation of maleic anhydride and to a sampling valve heated to 150°C on the first gas chromatograph. After that the gases passed through a water-cooled loop, where most of the maleic anhydride was condensed, and then to another sampling valve on the second gas chromatograph.

3. Catalyst

The catalyst used has been prepared as follows: H_2MoO_4 (14.4 g) was dissolved in diluted ammonia (350 cc) at 88°C to bring the final pH to 6.7. A solution of $MnCl_2 \cdot 4H_2O$ (17.1 g) in distilled water (350 cc) at 80°C was prepared; in the presence of a small amount of diluted ammonia the final pH was brought to 6.7. The manganese chloride solution was added into the ammonium molybdate solution while the latter was mixed vigorously; the final conditions were T = 85°C and pH = 5.5. The precipitate was dried at 120°C for 2 hr and later calcined at 500°C for 2 hr.

This preparation differs from that reported by other authors, such as Mann *et al.* (*6*) and permits one to obtain $MnMoO_4$ free from MnO_2 and MoO_3, at least as revealed by ir and X-ray analysis.

The ir spectrum of our catalyst is reported in Fig. 3. The *d* values and respective percent amounts, as determined by X rays are in the order: 1.7277 (6.3%); 1.7806 (6.3%); 1.9936 (6.4%); 2.2263 (5.32%); 2.3018 (9%); 2.3796 (6.9%); 2.5158 (9%); 2.7139 (17%); 2.7799 (5.32%); 2.8626 (11.7%); 3.2038 (10.7%); 3.2844 (5.32%); 3.3334 (16%); 3.4584 (100%); 3.6034 (8%); 3.8999 (14.35%); 5.7242 (2.66%); 6.8627 (5.32%), in agreement with data of Abrahams and Reddy (*11*). Diffuse reflectance spectra of the catalyst both calcined in air at 500°C for 1 hr and after reaction, showed no absorption in the visible region (the catalyst was white). Catalyst calcined at 550°C for 10 hr showed an absorption in the visible region at 580 nm but no modification in X ray and ir spectra; we attributed this absorption to the formation of MnO_2 or Mn_2O_3 on the surface (the catalyst was brown).

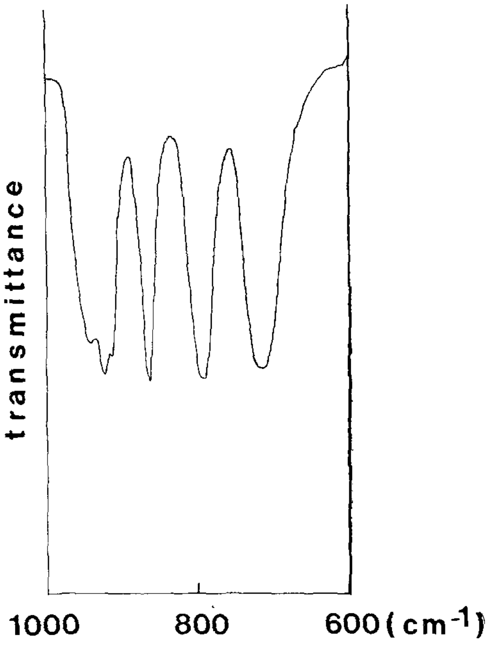

FIG. 3. IR spectrum of $MnMoO_4$.

4. Procedure

The mixing characteristics of the reactor were studied by carrying out the reaction at a constant temperature (390°C) and by obtaining a series of conversions at different agitation speeds (see Fig. 4). The lowest total feed rate used (25 cc/min)

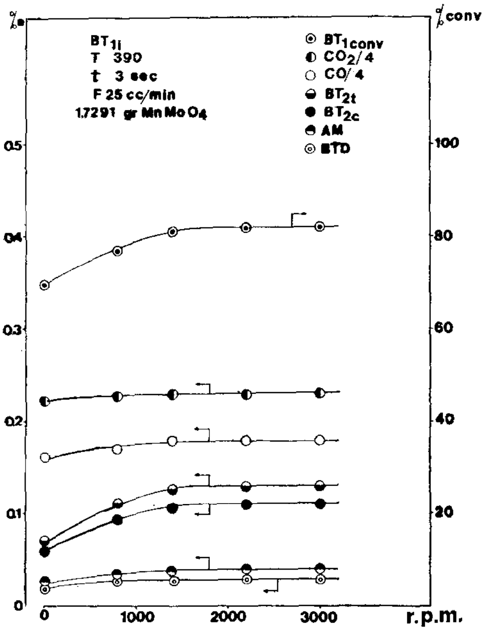

FIG. 4. Runs carried out at different agitation speeds (revolutions per minute). Meaning of the abbreviations used: $BT1_i$, *n*-butene-1 in the inlet stream; *T*, temperature; t, contact time; F, total gas flow; $BT2_t$, *trans*-butene-2; $BT2_c$, *cis*-butene-2; AM, maleic anhydride; BTD, butadiene; %e, molar percentage of the products in the exit gas; %conv., $\frac{\text{moles BT1 reacted}}{\text{moles BT1 feed}} \times 100$.

was chosen for this study. The operating region in which an apparent perfect mixing took place was assumed as the region in which conversion was independent of the rotation speed. All subsequent runs were performed in this region (rotation speed greater than 2200 rpm) and at 3000 rpm.

Some runs were carried out to determine the existence of homogeneous reactions at different temperatures and flow rates without catalyst. These runs have excluded the presence of noncatalytic gas-phase oxidation of *n*-butene-1.

The percentage of O_2 could be varied by addition of N_2 to the air in the reactor feed.

Each run was carried out according to the following procedure. While temperature was adjusted to the desired level, air was allowed to flow slowly in the reactor. After reaching the desired temperature, air and *n*-butene-1 flows were adjusted to the desired rates and kept at such rates for half an hour; in this way, the reactor could reach the steady state before making an analysis of the products.

RESULTS

1. *Oxidation in a Stirred Tank Flow Gradientless Reactor*

Figure 5 reports the outlet composition and conversion of *n*-butene-1 in oxidation runs carried out at different temperatures, the other kinetic parameters being constant. Conversion was calculated as moles *n*-butene-1 reacted /moles *n*-butene-1 feed × 100.

Figure 6 shows the percentage of products and the conversion of *n*-butene-1 vs contact time as a constant temperature (T = 380°C) and inlet composition of reactants.

Figure 7 shows the percentage of products and the conversion of *n*-butene-1 vs the concentration of *n*-butene-1 at constant

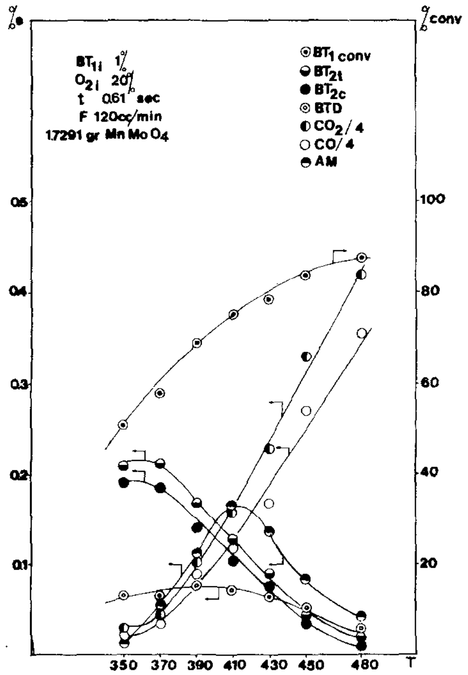

FIG. 5. Effect of temperature. For the meaning of the abbreviations, see Fig. 4.

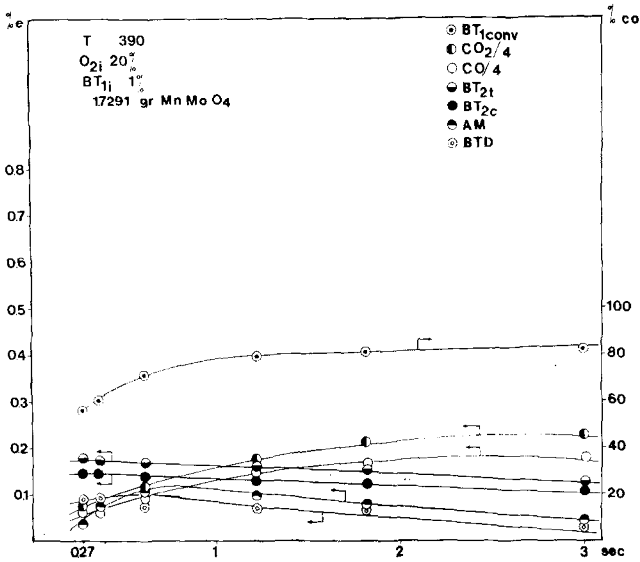

FIG. 6. Effect of contact time. For the meaning of the abbreviations, see Fig. 4.

temperature and contact time. In the run reported in Fig. 7 we have assumed that the concentration of oxygen is constant since it varied only from 18.37% to 19.27%.

In Fig. 8 we report the percentage of products and the conversion of *n*-butene-1 vs the concentration of oxygen. In order to deduce directly the kinetic order of the reactions with respect to oxygen, the concentration of *n*-butene-1 must be kept constant. This may be done by considering

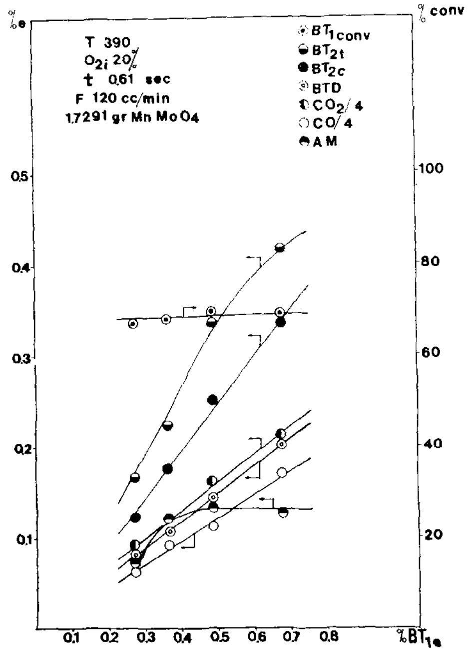

FIG. 7. Effect of *n*-butene-1. For the meaning of the abbreviations, see Fig. 4.

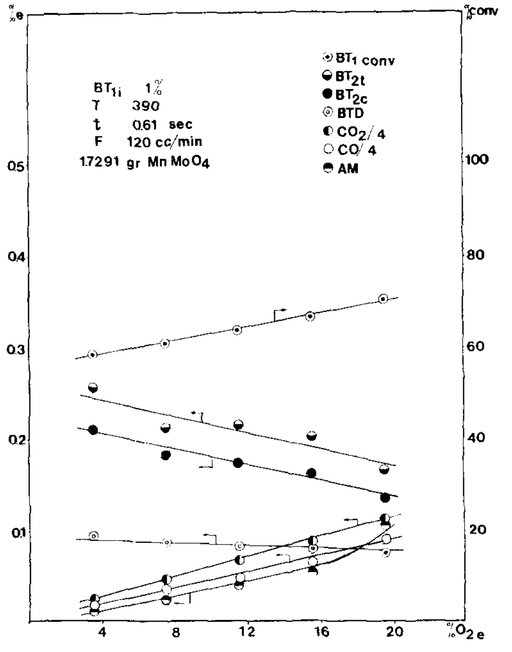

FIG. 8. Effect of % oxygen. For the meaning of the abbreviations, see Fig. 4.

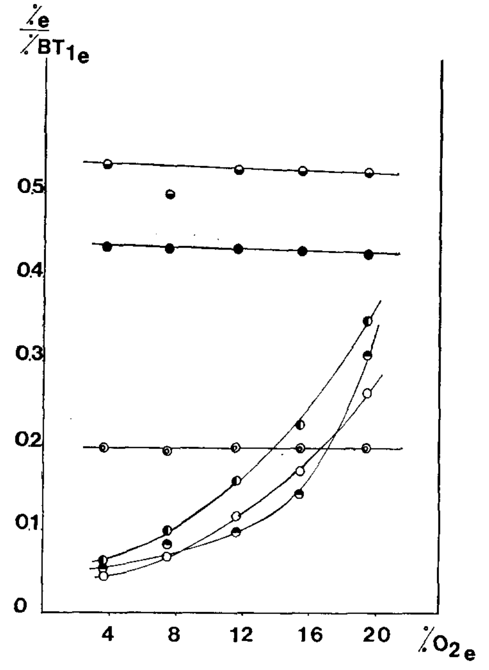

FIG. 9. Effect of % oxygen. Normalized data. The data of this figure have been normalized by dividing the values of the points of each run of Fig. 8 into the % of n-butene-1 in the exit stream of the respective run. In fact the order vs n-butene-1 for each considered reaction was unity in the concentration range of n-butene-1 in the exit stream to which the points of Fig. 8 refer. Consequently, for all the runs considered, Fig. 9 gives the order vs oxygen directly.

the data of Fig. 8 and the kinetic order with respect to n-butene-1.

The data of Fig. 8 have been normalized and plotted in Fig. 9. From the data of Figs. 7 and 9, we could deduce the order of the rate of formation of different products in respect of the reactants.

Attempts have been made to use *trans*-butene-2, *cis*-butene-2 and butadiene as reactants; we report the results of these runs in Table 1, together with comparative data concerning n-butene-1.

Among the high-boiling oxidized products, we have only reported maleic anhydride. Actually our calculations concerned also acetaldehyde, formaldehyde, acrolein, crotonaldehyde, which are present in the various runs although their content is never higher than 1% of the inlet butene.

TABLE 1

RUNS CARRIED OUT IN THE STIRRED-TANK REACTOR $T = 390°C$; $O_{2i} = 20\%$; $F = 120$ CC/MIN., CAT = 1.7291 g

% Input	Maleic anhydride yield × 100	[(CO + CO_2)/4] × 100 yield
n-butene-1		
1.205	11	21.7
2.09	6	18
trans-butene-2		
1.18	11.5	19
2.09	10.2	17.5
cis-butene-2		
1.2	10	21.2
2.07	8.5	18.3
butadiene		
1.22	25.1	18
2.06	17.5	20.2

2. *Oxidation in a Pulse Reactor*

In Fig. 10, we report the results obtained from oxidation runs carried out at different temperatures in a pulse reactor both in the presence and in the absence of gaseous oxygen.

Attempts have also been made to use CO and air as reactants; the catalyst, whether previously reduced with n-butene-1 or not, could not oxidize CO.

DISCUSSION

The results show that $MnMoO_4$ presents a fairly good selectivity in the catalytic vapor-phase oxidation of butenes to maleic anhydride. The best operating conditions adopted by us gave a molar yield (conversion × selectivity) to maleic anhydride of 22% (and a molar to butadiene of 13%); selectivity to maleic anhydride and to butadiene was 26.7 and 15.8%, respectively.

The Polyfunctional Nature of $MnMoO_4$

By varying the kinetic parameters, it was possible to check the following fourfold action of the $MnMoO_4$ catalyst: isomerization, dehydrogenation, oxidation

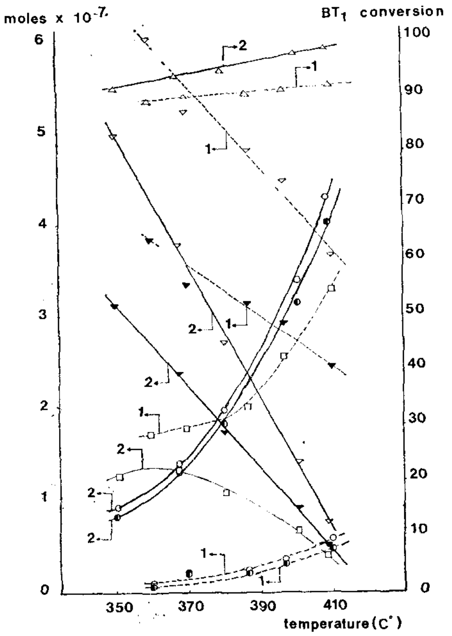

FIG. 10. Runs carried out in a microreactor with 1% of BT1 in the feed; contact time = 1.5 sec. (a) in the presence of oxygen (continuous lines marked with number 1) (b) in the absence of oxygen (dashed lines marked with number 2). Meaning of the symbols: △ conversion of *n*-butene-1, ▽ *trans*-butene-2, ▼ *cis*-butene-2, □ butadiene, ◐ CO/4, ● $CO_2/4$.

with oxygen insertion, oxidation with cleavage of C–C bonds.

The effect of contact time in Fig. 6 shows that the isomerization of 1-butene to 2-butene is very fast; therefore the oxidized products might be formed from 1-butene as well as from 2-butenes. However, on the basis of our data, we cannot deduce if the reactions are completed parallel or consecutive. Anyway, by a suitable choice of the kinetic parameters, we can find the fields where the single reaction predominates (see Table 2). The four classes of reactions also show different orders with respect to oxygen *n*-butene-1.

Isomerization

Figures 7 and 9 show that the production of isomers is first order with respect to *n*-butene-1 and lower than zero with respect to oxygen. The latter case may be due to the successive oxidation of isomers that occurs on increasing the partial pressure of oxygen.

Oxidative Dehydrogenation

The formation of butadiene is first order with respect to *n*-butene-1 and practically zero with respect to oxygen.

Insertion of Oxygen

The rate of production of maleic anhydride is about first order with respect to oxygen; it depends on the concentration of *n*-butene-1 when concentrations are lower than 0.4, and it is about zero order (with respect to *n*-butene-1) at higher concentrations.

Oxidation Cleavage of C–C Bonds

The formation of CO and CO_2 is first order with respect to both oxygen and *n*-butene-1.

The Nature of the Active Sites

The spectrum of the products obtained from *n*-butene-1 oxidation in a pulse reactor depends critically on the presence or the absence of oxygen in the feed.

TABLE 2
POLYFUNCTIONAL NATURE OF $MnMoO_4$

		Isomerization	Oxidative dehydrogenation	Oxidation with insertion of O_2 (formation of maleic anhydride)	Cleavage of C—C bonds and complete oxidation	
% O_2	0 ⊢——					——→ 20%
T °C	350 ⊢——					——→ 480°C
sec.	0.27 ⊢——					——→ 2 sec.

In the absence of oxygen the catalyst shows a high selectivity to butadiene

$$\left(\frac{\text{butadiene}}{n\text{-butene-1} - \Sigma\text{ butenes in exit gas}} \times 100 = 70\right)$$

which is typical of catalysts such as Bi–molybdates.

In the presence of oxygen the selectivity to butadiene is very low and rather large amounts of CO and CO_2 as well as traces of maleic anhydride have been observed. (The lower amount of maleic anhydride is quite probably due to mass and heat gradients which are not present in a stirred-tank flow reactor but can occur in a pulse reactor such as the one used in this case.) Therefore, the selectivity to butadiene is a typical property of lattice oxygen, while the formation of CO and CO_2 and maleic anhydride mainly depends on the presence of oxygen in the gas phase, as may be deduced from Fig. 10. Also for Bi–molybdates the formation of butadiene in the oxidation of *n*-butene-1 has been attributed to lattice oxygen, but no difference in the selectivity to butadiene was observed in the presence or in the absence of oxygen (*12*). Therefore, we can suppose that the properties of lattice oxygen responsible for selectivity to butadiene are similar both for $MnMoO_4$ and Bi–molybdates.

As reported in a previous paper (*13*) and in agreement with the oxidation mechanism proposed by Dewing (*14*) and Marion *et al.* (*15*), Mo=O groups are responsible in molybdates for the dehydrogenation of butenes to butadiene. Mo=O bonds were observed in Bi-molybdates (*8*).

In the case of $MnMoO_4$, too, ir spectra reveal the presence of Mo=O bonds at 900–940 cm^{-1} (*16*), which are more precisely due to dioxospecies (*17*) of molybdenum, together with two different types of $\mathrm{Me}\overset{\mathrm{O}}{\diagup\,\diagdown}\mathrm{Me}$ (bands at 700 cm^{-1} and at 800 cm^{-1}).

The differences observed between $MnMoO_4$ and Bi–molybdates in the oxidation carried out in the presence of oxygen show that the role of gaseous oxygen is different with these two catalyst. In the case of Bi–molybdates (*18, 19*) and also Fe–molybdate (*20*), the hypothesized role of oxygen is to oxidize the reduced catalyst. The mechanism advanced is the following:

$$\begin{aligned}
\mathrm{Mo^{VI}} + \text{hydrocarbon} &\rightarrow \mathrm{Mo^{V}} + \text{oxidized product}\\
\mathrm{Mo^{V}} + \mathrm{Bi^{III}}\ (\text{or } \mathrm{Fe^{III}}) &\rightarrow \mathrm{Mo^{VI}} + \mathrm{Bi^{III}}\ \text{reduced (or } \mathrm{Fe^{II}})\\
\mathrm{Bi^{III}}\ \text{reduced (or } \mathrm{Fe^{II}}) + \tfrac{1}{2}\mathrm{O_{2_{gas}}} &\rightarrow \mathrm{Bi^{III}}\ (\text{or } \mathrm{Fe^{III}})
\end{aligned}$$

In the first step the hydrocarbon is oxidized by $\mathrm{Mo^{VI}}$. In the second step a lattice redox reaction occurs between the reduced form of Mo and $\mathrm{Bi^{III}}$ or $\mathrm{Fe^{III}}$, respectively. In the third step $\mathrm{Bi^{III}}$ reduced or $\mathrm{Fe^{II}}$ are oxidized either by gaseous or adsorbed oxygen. Therefore, the hydrocarbon and oxygen interact with the catalyst on two different centers. This two-center mechanism seems very improbable for $MnMoO_4$ since Mn is in its lowest valence state and hence it cannot oxidize $\mathrm{Mo^{V}}$ or $\mathrm{Mo^{IV}}$. The difficulty of lattice redox process in $MnMoO_4$ is also shown by the higher temperature of the bulk reduction in a flow of H_2 namely 550°C as compared with 400°C for Bi–molybdates (*21*) and Fe–molybdates (*22*).

A two-center mechanism, as in the following, seems to us not so probable

$$\begin{aligned}
\mathrm{Mo^{VI}} + \text{hydrocarbon} &\rightarrow \mathrm{Mo^{V}} + \text{oxidized products}\\
\mathrm{Mn^{II}} + \tfrac{1}{2}\mathrm{O_2}\ \text{gas} &\rightarrow \mathrm{Mn^{III}}\ (\text{or } \mathrm{Mn^{IV}})\\
\mathrm{Mn^{III}} + \mathrm{Mo^{V}} &\rightarrow \mathrm{Mo^{VI}} + \mathrm{Mn^{II}}.
\end{aligned}$$

We think that this mechanism might be operating at higher temperature than 400°C. In fact, we reported that a surface modification occurs on $MnMoO_4$ catalyst only under very strong conditions (calcination in air at 550°C for 10 hr). An absorption in the visible region was observed in the diffuse reflectance spectrum, but there was no modification in the X-ray spectrum. We attributed this absorption to the presence of Mn in a high oxidation state, owing to the decomposition of $MnMoO_4$ on the surface through oxidation of surface Mn^{II} by gaseous oxygen. We think it is very probable that both hydrocarbon and oxygen react on the same center, respectively on Mo^{VI} and on the reduced form of Mo^{VI}, according to the following scheme:

$$\begin{aligned}
&Mo^{V\!I} + \text{butene} \rightarrow Mo^{V} + \text{butadiene}\\
&\quad Mo^{V} + O_{2(\text{gas})} \rightarrow Mo^{V}\text{-}O_{2(\text{ads})} \rightarrow Mo^{V\!I}\\
&\qquad\qquad\qquad\qquad \xrightarrow{+\ \text{hydrocarbon}} CO,\ CO_2,\ \text{maleic anhydride}
\end{aligned}$$

The hydrocarbon which reacts with the $(Mo^{V}\text{-}O_{2(ads)})$ center is quite probably butadiene. Evidence about the role of butadiene as an intermediate species in the formation of oxidized products can be gained from Table 1 as butadiene shows a higher yield to maleic anhydride, CO and CO_2 than *n*-butene-1 or butenes-2. In the following, Fig. 10 seems to confirm this opinion.

We propose that during the oxidation of the reduced form of Mo^{VI}, a form of adsorbed oxygen occurs that, either due to its particular nature or because it is adsorbed on the same center as the hydrocarbon, can account for oxidation to maleic anhydride, CO and CO_2. A monocenter mechanism like the one we propose must be present in MoO_3, so this catalyst should show a catalytic behavior similar to $MnMoO_4$.

In fact, in the oxidation of propylene by MoO_3, Peacock *et al.* (*19*) found a marked difference in selectivity according as to whether the oxidation is carried out in the presence or in the absence of oxygen. Moreover, MoO_3 catalyst in the oxidation of butene-1 gives a fairly good selectivity to maleic anhydride (*23*).

The form of chemisorbed oxygen we have hypothesized on $MnMoO_4$ shows a peculiar selectivity since it leads to maleic anhydride in the oxidation of *n*-butene-1 and is unable to oxidize CO.

With regard to the active sites in the isomerization, we think that they are acidic sites tied to Mn^{II}, by analogy with our suggestions for $Fe_2(MoO_4)_3$ (*20*) (Fe^{II} is the active site) and with hypotheses on the role of Mn^{II} in the acid behavior of $MnSO_4$ (*24*). However, we cannot exclude that Mo^{V} or Mo^{VI} might take some part in the isomerization.

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